

Establishment of background water quality conditions in the Great Zab River catchment

Ismaiel, Ismaiel Asad; Bird, Graham; McDonald, Morag; Perkins, William; Jones, Timothy

Environmental Earth Sciences

DOI:

[10.1007/s12665-017-7190-8](https://doi.org/10.1007/s12665-017-7190-8)

Published: 01/01/2018

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):

Ismaiel, I. A., Bird, G., McDonald, M., Perkins, W., & Jones, T. (2018). Establishment of background water quality conditions in the Great Zab River catchment: influence of geogenic and anthropogenic controls on developing a baseline for water quality assessment and resource management. *Environmental Earth Sciences*, 77(2), [50]. <https://doi.org/10.1007/s12665-017-7190-8>

Hawliau Cyffredinol / General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Establishment of background water quality conditions in the Great Zab River catchment: influence of geogenic and anthropogenic controls on developing a baseline for water quality assessment and resource management

Ismaiel Asad Ismaiel¹, Graham Bird^{1,*}, Morag A. McDonald¹, William T. Perkins², Timothy G. Jones³

¹School of Environment, Natural Resources and Geography, Bangor University, Bangor, Gwynedd, UK, LL57 2UW.

²Department of Geography and Earth Sciences, Aberystwyth University, Aberystwyth, Ceredigion, UK, SY23 3DB

³School of Biological Sciences, Bangor University, Bangor, Gwynedd, UK, LL57 2UW

*corresponding author. Email: g.bird@bangor.ac.uk, Te.: +44 01248 383222

ABSTRACT

The Great Zab River catchment is a major left-bank tributary of the River Tigris and drains a substantial part of the Kurdistan Region, an autonomous region of Northern Iraq. Within Kurdistan, the water resources of the Great Zab River catchment are under pressure from population increase and are utilized for potable, domestic and agricultural and industrial supply. As with many parts of the world, effective management of water resources within Kurdistan is hindered by a lack of water quality data and established background concentrations. This study therefore represents the first regional survey of river water chemistry for the Great Zab River catchment and presents data on the spatial and temporal trends in concentrations of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sr, Zn, NO_3^- , SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} , in addition to pH, electrical conductivity, dissolved oxygen and turbidity. As a tool for underpinning the management and monitoring of water quality, background concentrations were defined for the Great Zab catchment using three methods. The influences of geogenic and anthropogenic controls upon spatial and temporal trends in water chemistry are also evaluated. The influence of geogenic loading from underlying bedrock was identifiable within the observed spatial trends, with the most notable differences found between waters sampled from the relatively more volcanic-rich Zagros Zone to the north and those sampled from the lower catchment underlain by younger clay-, sand- and siltstones. The greatest anthropogenic influence, identifiable through elements such as Cl^- and NO_3^- , is present in the more highly-populated lower catchment. The background concentrations identified in the Great Zab catchment would be those expected as a result of geogenic loading with some anthropogenic influence and represent a more conservative value when compared to those such as the World Health Organization Maximum Admissible Concentration. However, background concentrations represent a powerful tool for identifying potential anthropogenic impacts on water quality and informing management of such occurrences.

KEY WORDS: ambient background; water quality; management; Kurdistan

INTRODUCTION

As noted by Adams and Chapman (2007), compared to organic substances, metals in surface waters pose significant regulatory challenges given that they may be sourced from natural geogenic loading as well as anthropogenic inputs, and that the latter may be highly spatially variable and diffuse in nature. Furthermore, anthropogenic inputs may stem from historical activities long-since ceased (e.g. Alpers et al., 2005).

A major step in developing a regulatory framework for surface water quality is the derivation of background concentrations (Oste et al., 2012). Determining a background concentration may be used to set a threshold value, which may allow instances of contamination of water to be identified (Panno et al., 2006). Background can be considered to be a concentration of a substance resulting from natural processes, uninfluenced by human activity (Reimann and Garrett, 2005). Given the spatially variability in factors determining geogenic metal loading to surface waters, 'global' background values are therefore of limited use (Oste et al., 2012). As a result, developing regional background concentrations can be seen as preferable. Given the difficulty in finding waters that have no anthropogenic 'signal' (Smith et al., 2003), the term 'ambient background concentrations' has been developed, whereby concentrations represent natural and low level anthropogenic inputs (Peters et al., 2012). Approaches to defining background concentrations in surface waters have been reviewed by detail by Oste et al. (2012).

Ensuring water quality is a key component of ensuring sufficient water supply as part of water resources management. This is particularly relevant to the provision of potable water supplies. Pressures on water quality have been noted in catchments and regions experiencing population and industrial growth (McDonald et al., 2011; McDonald et al., 2014).

The Kurdistan region is experiencing rapid increase in population. This combined with an increased urban population and improvements in living standards have resulted in pressures on water resources through impacts upon water quality (Alobaidy et al., 2010). These pressures are being felt, in conjunction with the threat posed from climate change, across the globe (Vörösmarty et al., 2000). The Great Zab River catchment represents one of the largest catchments in the Kurdistan Region, covering an area of approximately 40,643 km² and surface waters in the catchment provide water supply to a population of 1.8 million. Effective management of water resources through legislative control on water quality is currently being restricted by a lack of national water quality guidelines (Shareef and Muhamad, 2008). Whilst there has been some study of water quality in particular parts of the catchment (e.g. Abdulwahid, 2013; Shareef et al., 2009; Shareef and Muhamad, 2008; Toma, 2011a; Toma, 2011b), there has been no attempt to establish baseline water chemistry and define

background concentrations that may act as a means of evaluating water quality, and which may form the basis for the development of appropriate legislative guidelines.

The aims of this study are therefore to address this knowledge gap by determining ambient background concentrations for the Great Zab River catchment for 16 metals, 5 anions, pH, electrical conductivity (EC), dissolved oxygen (DO) and turbidity and to evaluate the spatial and seasonal trends in water quality within the catchment.

STUDY AREA

Kurdistan occupies an area of 40,643 km² and a population growth rate is 2.7% per annum (Ministry of Planning, 2011), notably in the cities of Erbil, the capital city, Sulaimaniya and Dohuk, is placing pressure upon water resources. Stevanovic and Lurkiewicz (2009) report that that population growth has led to the decline in the per capita availability and use of water resources. According to the Ministry of Planning/KRG (2011), the quantity of water produced on a daily basis is 924,600 m³, while daily demand totals approximately 1.25 million m³. Therefore, the present water supply deficit is 325,400 m³ per day, i.e. 26% of total demand and 35% of total quantity produced at present.

The Great Zab River catchment covers an area of approximately 40,300 km², with 13,708 km² within Kurdistan and the remainder in Turkey. The Great Zab River is a left bank tributary of the River Tigris, with confluence downstream of Mosul. The flow regime of the Great Zab River is strongly influenced by annual snowmelt, with the highest monthly mean discharges occurring in the early summer months (Saleh, 2010). Within Kurdistan, the Great Zab catchment sits within three major geological zones (Figure 1). To the northeast, the Zagros Zone comprises predominantly folded limestones with some felsitic volcanics. The Imbricated and High-fold zones comprise Cretaceous-age carbonates in a range of different formations. A detailed description of these has been produced by Sissakian (2013), however, in summary these formations comprise predominantly limestone that has been variably pervaded by dolomite, marl and shale. The lower portion of the catchment lies within the Foothill zone (Figure 1), dominated by late Miocene to Pleistocene-aged sandstones, siltstone and claystone (Sissakian, 2013). The region at the boundary of the High-fold and Foothill zones comprises a number of formations of generally Paleocene and Eocene age that comprise dolomitic limestones and, particularly to the northwest, thick basaltic lavas (Sissakian, 2013).

METHODS

Samples of river water were collected from 62 sites in February 2014 and June 2014 (Figure 1). Sample sites were selected to best balance the demands of ease of access and spatial coverage, with sample sites focusing mainly upon road-river intersections (c.f. Bird et al., 2010). In the field, samples were filtered through 0.45 μm cellulose nitrate filter membranes, acidified with 50% HNO_3 and placed on ice in acid-washed Nalgene bottles. Samples were stored below 5°C prior to analysis. Concentrations of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sr, Zn were determined by Inductively Coupled Plasma Mass Spectrometry (Agilent Technologies 7700). Analytical accuracy was assessed through the analysis of the NIST1643 certified reference material and analytical precision through the repeat analysis ($n = 10\%$ of total sample number) of a randomly selected sample. Data for analytical quality control are given in Table 1. Samples were analysed by ion chromatography for their NO_3^- , SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} content. A Thermo Fisher AS22 anion exchange column was used for the separation of SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} . The mobile phase was 4.5 mM sodium carbonate/1.4 mM sodium bicarbonate and flow rate 1.2 ml/min. Suppression was achieved using a Metrohm Suppressor Module, supplied with a 150 mM sulphuric acid/0.1 M oxalic acid/acetone mix and ultrapure water. Inorganic anions were detected using a suppressed conductivity detector. All solutions were prepared in ultrapure water with a specific resistance of (18.2) $\text{M}\Omega\text{ cm}$ (Millipore, Molsheim, France). Analytical accuracy on anion analyses (Table 1) was assessed through the analysis of standard solutions and analytical precision through the repeat analysis ($n = 10\%$ of total sample number) of a randomly selected sample.

In the field, measurements of pH (Hanna Instruments HI991003), electrical conductivity (Hanna Instruments HI8733), dissolved oxygen (PDO520) and turbidity (Hanna Instruments HI93703) were made at the time of sampling.

RESULTS AND DISCUSSION

Water chemistry

A summary of minimum, mean, median and maximum values is provided for cations (Figure 2), anions (Figure 3) and pH, EC, DO, turbidity (Figure 4). Global median and World Health Organization (WHO) Maximum Admissible Concentrations (MACs) also plotted in order to provide context for the data from Kurdistan. WHO MACs are appropriate for potable water, which is consistent with the Great Zab River, and provides an indication of water quality in relation to human health. In addition, percentage cumulative frequency plots of the water chemistry data for cations (Figure 5) and anions, pH, EC, DO, turbidity (Figure 6) show the frequency distribution of the parameters in summer and winter. Arsenic, and Hg were non-detectable in all samples.

In comparison to world median values, cation concentrations in the Great Zab catchment vary by metal (Figure 2). All Li and Ca concentrations are greater than the world median value, whilst the third quartile concentration for Ba is greater than the world median concentration. Third quartile concentrations for Cu, Zn and Pb are lower than the respective world median concentrations. For metals for which a WHO MAC has been defined, all concentrations in the Great Zab catchment fall below these.

All anion concentrations measured in the Great Zab catchment fall below their respective WHO MACs (Figure 3). All F^- and NO_2^- concentrations measured in the Great Zab catchment fall below world median concentrations, however a majority of sites had SO_4^{2-} concentrations in excess of the world median. The median Cl^- concentration in the Great Zab (6.7 mg l^{-1}) is largely similar to the world median concentration of 8.3 mg l^{-1} .

The pH of river water ranges from mildly acidic (5.6) to mildly alkaline (8.9). The turbidity of water ($1.7\text{--}65 \text{ NTU}$) indicate that in general river water in Great Zab River catchment contains relatively low concentrations of suspended organic and inorganic material. Electrical conductivity ranges from 200 to $1028 \mu\text{S cm}^{-1}$ with a median value of $375 \mu\text{S cm}^{-1}$.

A Pearson Product Moment correlation was performed to evaluate bivariate relationships between water chemistry parameters. The full correlation matrix is included as Supplementary Material and Fe, As and Hg were not included in the analysis due to the high number of non-detectable concentrations. Statistically significant correlations between cations and anions are relatively rare, notable exceptions being between SO_4^{2-} ($r = 0.408$) and NO_3^- ($r = 0.441$) and Ba; both significant at $\alpha = 0.01$. Statistically significant correlation between cations and between anions are more frequent. With respect to cations, significant correlations exist between metals in the same groups, such as between the transition metals. Particularly strong correlations exist between Ni and Co ($r = 0.801$), Cu ($r = 0.659$) and Zn ($r = 0.816$). For alkaline earth metals, strong correlation relationships exist between Ca and Sr ($r = 0.822$) and Ba ($r = 0.349$). Significant correlations exist between a number of anions (see supplementary data), being strongest between F^- and SO_4^{2-} ($r = 0.637$). There are relatively few significant correlations between elemental concentrations and pH; Ca, Ba, Cl^- and NO_3^- being exceptions. Dissolved oxygen concentrations are correlated with PO_4^{3-} and SO_4^{2-} ($\alpha = 0.01$).

In order to establish whether water chemistry differs significantly between summer (lower flow conditions) and winter (generally higher flow conditions), data collected in February 2014 and June 2014 were compared using a one way ANOVA on log-transformed data, using a significance threshold of $\alpha = 0.05$. Results (Table 2) indicate that concentrations of Ca, Li, Mo are higher in the

winter than summer (statistically significant at $\alpha = 0.05$), whilst concentrations of Zn, SO_4^{2-} , F^- , Cl^- , and PO_4^{3-} are higher in the summer than winter (statistically significant at $\alpha = 0.05$). Seasonal differences for other analytes were not statistically significant. Higher concentrations of a number of elements during winter (higher discharge conditions) in the Great Zab catchment suggests enhanced delivery from the riparian zone via a combination of surface and sub-surface flows. Calcium, Li and SO_4^{2-} concentrations have been found to be consistently higher than world median concentrations.

The relationship between water quality and river discharge is a potentially complex scenario. Previous studies (e.g. Garbarino et al., 1995) have reported generally higher concentrations of metals under low flow conditions due to a lower degree of physical dilution that occurs during periods of low discharge. In addition, higher discharge conditions can result in a reduction in dissolved concentrations due an increase in sorption process due to higher suspended sediment concentrations. However, conversely other studies (e.g. Gundersen and Steinnes, 2001) have demonstrated that periods of higher discharge can yield higher metal concentrations due to enhanced delivery of substances to the river channel from run-off and the potential activation of point sources. What is apparent is that different elements can display different relationships with discharge, as noted in a study of Southeast Asian rivers by Chanpiwat and Sthiannopkao (2014).

In an attempt to evaluate the spatial trends in water quality, samples were grouped based upon the major underlying geological units identified in the Great Zab catchment. The groups were identified as: 1) Zagros Zone, 2) the Imbricated/High-folded Zone and 3) the Foothill Zone (Figure 1). The grouping by underlying geology, reflects the importance of geogenic loading in determining surface water chemistry (Drever, 1997). Log-transformed data were analysed using a one way ANOVA, using a significance threshold of $\alpha = 0.05$. The most frequent differences were found between water chemistry in samples collected from the Zagros and Foothill Zones, with 13 parameters showing a statistically significant difference (Table 2). Five and 7 parameters, respectively showed statistically significant differences between the Zagros and Imbricated/High-fold Zones and Imbricated/High-fold and Foothill Zones. The greater statistical similarity of water chemistry sampled in the Imbricated/High-fold and Foothill Zones will reflect the greater similarity in bedrock geology between these areas than compared with the Zagros Zone. The influence of geology on water chemistry is exemplified by Ca and Sr concentrations; these are found to be significantly higher in waters within the Imbricated/High-fold and Foothill Zones than in the Zagros Zones (Table 2). Average Sr concentrations in water with the Imbricated/High-fold ($542 \mu\text{g l}^{-1}$) and Foothill Zones ($683 \mu\text{g l}^{-1}$) are at least twice as high as in the Zagros Zone ($243 \mu\text{g l}^{-1}$). Average Ca concentrations are c. 10 mg l^{-1} lower in the Zagros Zone compared to the Imbricated/High-fold and Foothill Zones. This

reflects the abundant carbonate bedrocks, notably limestone and dolomitic limestone, which are the main sources of Sr to stream water in particular, whilst the bedrock of Zagros Zone is relatively carbonate poor.

Chloride and NO_3^- show a statistically significant difference between the Foothill Zone (the lower Great Zab catchment) and the two upstream zones (Table 2). Concentrations of Cl^- and NO_3^- are significantly higher in the lower catchment (Figure 7), as indicated by mean concentrations of 14.2 and 6.8 mg l^{-1} , respectively, which are twice as high as those for the Zagros and Imbricated/High-fold Zones upstream. Chloride and NO_3^- are two elements for which higher concentrations in river water, and particularly within-catchment variability, can be the result of anthropogenic inputs, such as from agricultural activity in the case NO_3^- (Randall and Mulla, 2001). Importantly, the amount of anthropogenic activity is greatest in the lower Great Zab catchment, the part of the catchment containing the highest Cl^- and NO_3^- levels. Whilst concentrations are below respective WHO MACs, the data exemplify and indicate that whilst geogenic inputs are important in explaining large scale variability in water chemistry, the spatially variable influence of anthropogenic activity is an important contributor to the water chemistry of the Great Zab catchment.

Quantifying background conditions

Establishing background geochemical conditions, provides a potentially valuable regulatory tool for evaluating water quality. However, given the difficulty in locating 'pristine' water bodies that have no anthropogenic influence, as reviewed by Peters et al. (2012), a range of approaches have been utilized to quantify background conditions in river catchments. Peters et al. (2012) used a low percentile of water quality data to provide a relatively conservative estimate of background, or what can be termed 'ambient background'. In contrast, other approaches have utilized higher percentile, such as the 90th percentile value (Fraters et al., 2001).

To evaluate the potential influence of the approach used, three different approaches were taken. Firstly, background conditions were calculated as the 10th percentile value (Peters et al., 2012) of the whole dataset from the Great Zab River catchment (Table 3). Secondly, based upon the analysis of Q-Q plots of NO_3^- concentrations, utilized as an anthropogenic marker, and other water quality parameters (Figure 8), the 95th percentile was identified as a point where the distributions differ (Helsel and Hirsch, 2002). Therefore this is indicative of a different sample population above the 95th percentile and can be interpreted as a separation of geogenic and anthropogenic components (Table 3). Finally, following the method of Davies (1983) background concentrations were estimated using

254 regression analysis of % cumulative frequency curves of log10 concentrations from the sample
255 population (Table 3).

256 Generally, of the three approaches, the 10th percentile concentrations are always the lowest (Table
257 3), with the exception of Ca and Sr, for which the regression-derived concentrations are lowest. The
258 10th percentile concentrations have been described by Peters et al. (2012) as reflecting ambient
259 background conditions that, in relation to the Great Zab catchment, would be expected resulting
260 from natural, geogenic inputs and low level anthropogenic activity. However, utilizing NO₃⁻
261 concentrations as an anthropogenic marker, suggest that the proportion of the sample population
262 that could be considered as geogenic is much larger, equating to the 95th percentile value, and that
263 background concentrations could potentially be established at higher concentrations.

264 Given that background concentrations may be used as an indicator of water quality, the background
265 concentrations can be compared to WHO MACs (Table 3). All background concentrations in the
266 Great Zab, determined by the three methods used, are lower than WHO MACs. In some case,
267 background concentrations are orders of magnitude lower, for example in the case of Cu and Zn
268 (Table 3). The comparison to WHO MACs suggests that the background concentrations defined by
269 this study can be viewed as very conservative if used as a guide for water quality based upon risks
270 posed to human health. It is not suggested that the background concentrations derived here are
271 adopted as a measure to protect human health, however, the concentrations quantified may act as
272 valuable guide for identifying instances for anthropogenic pollution within the Great Zab catchment.

273 Variations in water chemistry within the catchment would mean that the instances of enrichment
274 above background concentrations varies between waters from the Zagros, Imbricated/High Fold and
275 Foothill Zones. By way of example, comparison of Li, Ba, F⁻ and NO₃⁻ concentrations, which have
276 been shown to differ significantly between the three zones (Table 2), suggests that instances of
277 elevation above background concentrations vary between zone and element (Figure 9). Highest
278 NO₃⁻ concentrations occur in the Foothill Zone, in waters from the Great Zab River itself, but also its
279 tributaries, the Khazir River and the Gomal. NO₃⁻ concentrations in 7% of samples from Foothill zone
280 exceed the 95th percentile-defined background value, but samples from the Zagros and
281 Imbricated/High Fold Zones do not. Conversely, Li and F⁻ concentrations in the Zagros Zone, in 9%
282 and 7% of samples respectively, exceed the 95th percentile-defined background value, with all
283 samples in the two downstream zones falling below. These data further highlight that spatial trends
284 in water chemistry, including the occurrence of relative elevation in concentrations, are likely to
285 reflect both geogenic influences operating at larger spatial scales and site-specific conditions,

particularly point sources associated with anthropogenic activity, that vary between different water quality parameters.

CONCLUSIONS

This study has conducted and presented data for the first regional survey of river water chemistry for the Great Zab River catchment, a major left-bank tributary of the River Tigris. Data analysis has shown that concentrations in river water of Ca, Li, Mo, Zn, F⁻, Cl⁻, SO₄²⁻ and PO₄³⁻ are significantly different during summer and winter sampling periods, however, there are variations in terms of when concentrations are highest for different elements. The Great Zab catchment can be divided into three major geological units, and the influence of bedrock geology upon surface water chemistry is evidenced by differences in elemental concentrations in waters sampled from the different units. In addition, whilst elemental concentrations in the Great Zab are below WHO MACs, a potential anthropogenic influence on water chemistry is identifiable through the location of highest elemental concentrations. The lower catchment, which is most highly populated contains highest elemental concentrations and represent areas of concern for water resources management.

Background concentrations for the Great Zab catchment have been quantified using the 10th and 95th percentile concentrations and a regression analysis. These concentrations could be used as the basis for establishing water quality norms for the catchment and potentially the broader Kurdistan region. Comparison to WHO MACs, which provide human-health oriented guidelines for water quality, indicates that the use of a background concentration as a guide for water quality management, would produce much more conservative and stricter quality limits. This suggests that there is a potentially significant difference between background concentrations, which may be used to identify instances of contamination within a catchment and guidelines that establish potential threats to human health. The use of a guideline such as a WHO MAC as a measure of water quality in water quality assessments may actually mask instances of poor water quality that are identified via the establishment of a catchment-wide background concentrations.

ACKNOWLEDGEMENTS

IAI acknowledges PhD funding provided by the Kurdistan Ministry of Higher Education and Scientific Research.

FIGURE CAPTIONS

Figure 1. Location map showing the Great Zab catchment within Kurdistan, major study rivers, sample sites and major geological units.

Figure 2. Minimum, median and maximum concentrations for cations in river water plotted with global median and World Health Organization (WHO) Maximum Admissible Concentrations (MACs), where determined.

Figure 3. Minimum, median and maximum concentrations for anions in river water plotted with global median and World Health Organization (WHO) Maximum Admissible Concentrations (MACs), where determined.

Figure 4. Minimum, median and maximum values for pH, EC, DO and turbidity in river water plotted with global median and average values and World Health Organization (WHO) Maximum Admissible Concentrations (MACs), where determined.

Figure 5. Cumulative frequency plots of cation concentrations in the Great Zab catchment during winter and summer seasons.

Figure 6. Cumulative frequency plots of anion concentrations and pH, EC, DO and turbidity in the Great Zab catchment during winter and summer seasons.

Figure 7. NO_3^- and Cl^- concentrations in the Great Zab catchment plotted as proportional circles.

Figure 8. Q-Q plots of NO_3^- (as an anthropogenic tracer) and Li, Zn and Sr concentrations in the Great Zab catchment.

Figure 9. Minimum, median and maximum concentrations of Li, F^- , Ba and NO_3^- determined in the river water from three geological zones within the Great Zab catchment. Background concentrations determined by three different methods are also plotted.

344 REFERENCES

- 345 Abdulwahid, S., 2013. Water quality index of delizhiyan springs and Shawrawa River within Soran
346 district, Erbil, Kurdistan Region of Iraq. *Journal of Applied Environmental and Biological Sciences* 3,
347 40-48.
- 348 Adams, W.J., Chapman, P.M., 2007. Assessing the hazards of metals and inorganic substances in
349 aquatic and terrestrial systems. Proceeding from the Workshop on Hazard Identification Approach
350 for Metals and Inorganic Metal Substances. Pensacola Beach, Florida. CRC Press,, London.
- 351 Alobaidy, A., Abid, H., Maulood, B., 2010. Application of water quality Index for assessment of Dokan
352 lake ecosystem, Kurdistan region- Iraq. *Journal of Water Resources and Protection* 2, 792-798.
- 353 Alpers, C.N., Hunerlach, M.P., May, J.T., Hothem, R.L., 2005. Mercury Contamination from Historical
354 Gold Mining in California. United States Geological Survey, Sacramento, p. 6.
- 355 Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air and Geochemical Cycles*. Prentice
356 Hall, Upper Saddle River.
- 357 Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010.
358 Contaminant-metal dispersal in mining-affected river catchments of the Danube and Maritsa
359 drainage basins, Bulgaria. *Water Air and Soil Pollution* 206, 105-127.
- 360 Chanpiwat, P., Sthiannopkao, S., 2014. Status of metal levels and their potential sources of
361 contamination in Southeast Asian rivers. *Environmental Science & Pollution Research* 21, 220-233.
- 362 Davies, B.E., 1983. A graphical estimation of the normal lead content of some British soils. *Geoderma*
363 29, 67-75.
- 364 Drever, J.I., 1997. *The Geochemistry of Natural Waters*, 3rd ed. Prentice Hall, Upper Saddle River.
- 365 Fraters, B., Bounmans, L.J.M., Prins, H., 2001. Achtergrondconcentraties van 17 sporenmetalen in
366 het groundwater van Nederland (in Dutch). RIVM, Bilthoven, The Netherlands. Report no.
367 711701017.
- 368 Garbarino, J.R., Hayes, H.C., Roth, D.A., Antweiler, R.C., Brinton, T.I., Taylo, H.E., 1995. Heavy metals
369 in the Mississippi River, in: Meade, R.H. (Ed.), *Contaminants in the Mississippi River, 1987-92*. U.S.
370 Geological Survey Circular 1133, Reston, Virginia.
- 371 Gundersen, P., Steinnes, E., 2001. Influence of temporal variations in river discharge, pH, alkalinity
372 and Ca on the speciation and concentration of heavy metals in some mining polluted rivers. *Aquatic*
373 *Geochemistry* 7, 173-193.
- 374 Helsel, D.R., Hirsch, R.M., 2002. *Statistical Methods in Water Resources Techniques of Water*
375 *Resources Investigations. Book 4, chapter A3* U.S. Geological Survey.
- 376 Ivanov, V.V., 1996. *Ekologicheskaya geokhimiya elementov* (in Russian). *Ekologia* 1-6.
- 377 McDonald, R.I., Green, P., Balk, D., Fekete, B.M., Revenga, C., Todd, M., Montgomery, M., 2011.
378 Urban growth, climate change, and freshwater availability. *Proceedings of the National Academy of*
379 *Sciences of the United States of America* 108, 6312-6317.
- 380 McDonald, R.I., Weber, K., Padowski, J., Floerke, M., Schneider, C., Green, P.A., Gleeson, T., Eckman,
381 S., Lehner, B., Balk, D., Boucher, T., Grill, G., Montgomery, M., 2014. Water on an urban planet:
382 Urbanization and the reach of urban water infrastructure. *Global Environmental Change-Human and*
383 *Policy Dimensions* 27, 96-105.
- 384 Ministry of Planning, 2011. *Regional Development Strategy for Kurdistan Region 2012-2016*.
385 Kurdistan Region Government (KRG), Erbil.
- 386 Oste, L., Zwolsman, G.J., Klein, J., 2012. Methods to derive natural background concentrations of
387 metals in surface water, and an application of two methods in a case study. *Deltares report*
388 1206111.005, Utrecht, p. 104.
- 389 Panno, S.V., Kelly, W.R., Martinsek, A.T., Hackley, K.C., 2006. Estimating background and threshold
390 nitrate concentrations using probability graphs. *Groundwater* 44, 697-709.
- 391 Peters, A., Merrington, G., Crane, M., 2012. Estimation of background reference concentrations for
392 metals in UK freshwaters. *Water Framework Directive - United Kingdom Technical Advisory Group*,
393 p. 49.

Randall, G.W., Mulla, D.J., 2001. Nitrate nitrogen in surface waters as influenced by climatic conditions and agricultural processes. *Journal of Environmental Quality* 30, 337-344.

Reimann, C., de Caritat, P., 1998. *Chemical Elements in the Environment: factsheets for the geochemist and environmental scientist*. Springer-Verlag, Berlin.

Reimann, C., Garrett, R.G., 2005. Geochemical background - concept and reality. *Science of the Total Environment* 350, 12-27.

Saleh, D.K., 2010. Stream gage descriptions and streamflow statistics for sites in the Tigris River and Euphrates River basins, Iraq. U.S. Geological Survey, Reston, Virginia, p. 147.

Shareef, K., Muhamad, S., Shekhani, N., 2009. Physical and chemical status of drinking water from water treatment plants on Great Zab River. *Journal of Applied Science and Environmental Management* 13, 89-92.

Shareef, K.M., Muhamad, S.G., 2008. Natural and drinking water quality in Erbil, Kurdistan. *Current World Environment* 3, 227-238.

Sissakian, V.K., 2013. Geomorphology and morphometry of the Greater Zab River Basin, North of Iraq. *Iraqi Bulletin of Geology and Mining* 9, 21-49.

Smith, R.A., Alexander, R.B., Schwarz, G.E., 2003. Natural background concentrations of nutrients in streams and rivers of the conterminous United States. *Environmental Science & Technology* 37, 3039-3047.

Stevanovic, Z., Iurkiewicz, A., 2009. Groundwater management in northern Iraq. *Hydrogeology Journal* 17, 367-378.

Toma, J., 2011a. Limnological study in Dokan Lake, Kurdistan region of Iraq. *Journal of Environmental Studies* 6, 1-12.

Toma, J., 2011b. Physical and chemical properties and Algal composition of Derbendikhan Lake, Sulaimania, Iraq. *Current World Environment* 6, 17-27.

Vörösmarty, C.J., P, G., Salisbury, J., Lammers, R.B., 2000. Global water resources: vulnerability from climate change and population growth. *Science* 289, 284-288.

434 Table 1. Analytical quality control data for laboratory analyses.

	Certified	Measured	% Accuracy	% Precision
As	60.5±0.7	40.5	33	6.6
Ba	544.2±5.8	504	7.3	1.9
Ca	32300±110	34100	5.6	3.6
Cd	6.6±0.07	5.7	13.8	n.d.
Co	27.1±0.32	20.4	24.5	1
Cr	20.4±0.24	15.9	21.7	1.8
Cu	22.8±0.31	39.6	74	1.8
Fe	98.1±1.4	97.6	0.5	4.9
Hg	-	-	-	n.d.
Li	17.4±1.7	9.3	46.3	0.9
Mn	38.9±0.45	34.9	10.4	3.6
Mo	121.4±1.3	120.9	0.4	0.7
Ni	62.4±0.69	62.4	0	0.7
Pb	19.6±0.21	18.7	4.8	n.d.
Sr	323.1±3.6	298.6	7.6	0.2
Zn	78.5±2.2	32.3	58.8	2.2
NO ₃ ⁻	-	-	4.4	2.5
SO ₄ ²⁻	-	-	7.9	2.1
F ⁻	-	-	3.5	5.8
Cl ⁻	-	-	11.5	3.4
PO ₄ ³⁻	-	-	0.5	1.9

435

436

437

438

439

440

441

442

443

444

Table 2. Results of a one-way ANOVA for temporal trends. Bold indicates significant at $\alpha = 0.05$. * denotes mean summer concentration is higher than mean winter concentration. ** denotes mean winter concentration is higher than mean summer concentration.

Parameter	P value (Seasonal)	P value (Spatial)		
		Z ¹ vs I/HF ²	Z v FZ ³	I/HF v FZ
As	N/A	N/A	N/A	N/A
Ba	0.486	0.888	0.000	0.000
Ca	0.000**	0.009	0.001	0.625
Cd	0.224	0.210	0.944	0.275
Co	0.986	0.711	0.299	0.025
Cr	0.719	0.063	0.653	0.270
Cu	0.487	0.210	0.772	0.500
Fe	0.224	0.233	0.455	0.726
Hg	N/A	N/A	N/A	N/A
Li	0.029**	0.000	0.000	0.855
Mn	0.223	0.980	0.455	0.726
Mo	0.036**	0.000	0.000	0.596
Ni	0.256	0.169	0.946	0.212
Pb	N/A	0.424	0.708	0.792
Sr	0.642	0.019	0.001	0.441
Zn	0.031*	0.311	0.801	0.629
NO ₃ ⁻	0.180	0.746	0.000	0.000
SO ₄ ²⁻	0.000*	0.651	0.000	0.000
F ⁻	0.000*	0.024	0.005	0.734
Cl ⁻	0.017*	0.771	0.008	0.000
PO ₄ ³⁻	0.000*	0.886	0.735	0.936
Turbidity	0.769	0.650	0.963	0.764
DO	0.000*	0.801	0.996	0.686
EC	0.563	0.119	0.021	0.626
pH	0.000**	0.413	0.014	0.000

¹Zagros Zone

²Imbricated/High-folded Zone

³Foothill Zone

Table 3. Background conditions defined for the Great Zab catchment. WHO MAC and world median concentrations also given for comparison. Concentrations in $\mu\text{g l}^{-1}$ unless stated.

	10 th percentile	95 th percentile	Regression analysis	WHO MAC	World median
Li	0.7	11.5	2.3	-	0.2 ¹
Ca	26.1 mg l ⁻¹	67 mg l ⁻¹	22 mg l ⁻¹	-	¹ 12 mg l ⁻¹
Cr	0.2	1.7	0.3	50	0.7 ¹
Mn	1.4	14.6	3.6	400	4 ¹
Fe	0.8	26.9	2.1	300	40 ¹
Co	0.1	0.5	0.1	-	0.3 ¹
Ni	0.9	7.2	1.7	70	0.3 ¹
Cu	0.2	14.8	0.5	2000	3 ¹
Zn	1.2	17.7	8.1	3000	15 ¹
As	n/d	n/d	n/d	10	4 ¹
Sr	161	1650	154	-	500 ¹
Mo	0.2	3.3	0.4	70	0.5 ¹
Cd	<0.01	0.01	<0.01	3	0.02 ¹
Ba	21	108	21	700	20 ¹
Hg	n/d	n/d	n/d	6	0.05 ¹
Pb	0.1	1.8	0.2	10	3 ¹
Cl ⁻	2.2 mg l ⁻¹	31.5 mg l ⁻¹	3.2 mg l ⁻¹	² 250 mg l ⁻¹	³ 7.8 mg l ⁻¹
SO ₄ ²⁻	13.6 mg l ⁻¹	105 mg l ⁻¹	15.9 mg l ⁻¹	² 250 mg l ⁻¹	⁴ 8.3 mg l ⁻¹
F ⁻	0.04 mg l ⁻¹	0.4 mg l ⁻¹	0.1 mg l ⁻¹	1.5 mg l ⁻¹	³ 0.1 mg l ⁻¹
NO ₃ ⁻	1.2 mg l ⁻¹	11.2 mg l ⁻¹	6.9 mg l ⁻¹	50 mg l ⁻¹	³ 1 mg l ⁻¹
PO ₄ ³⁻	<0.01 mg l ⁻¹	0.3 mg l ⁻¹	mg l ⁻¹	-	³ 0.03 mg l ⁻¹

¹Reimann and de Caritat (1998)

²Based upon acceptable taste. A health-based limit has not been established.

³Ivanov (1996)

⁴Berner and Berner (1996)

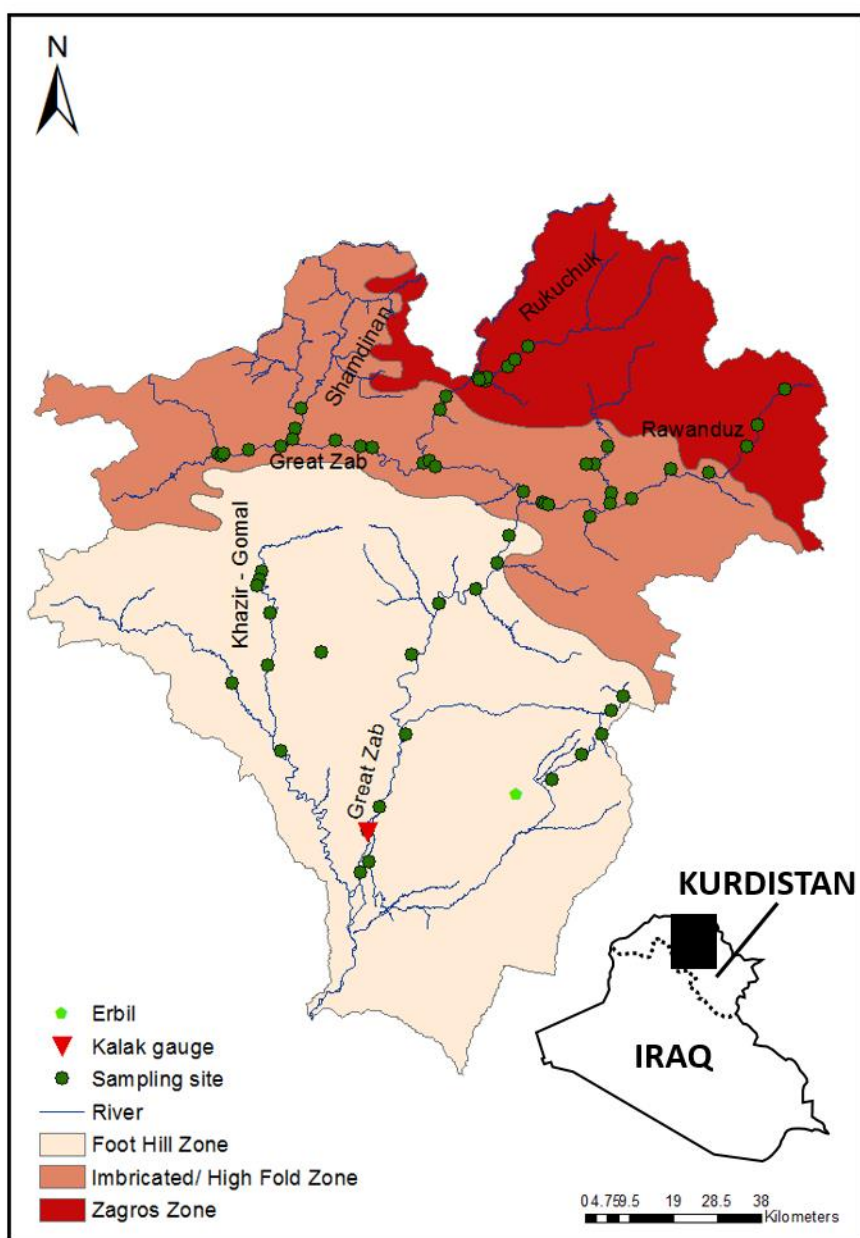


Figure 1.

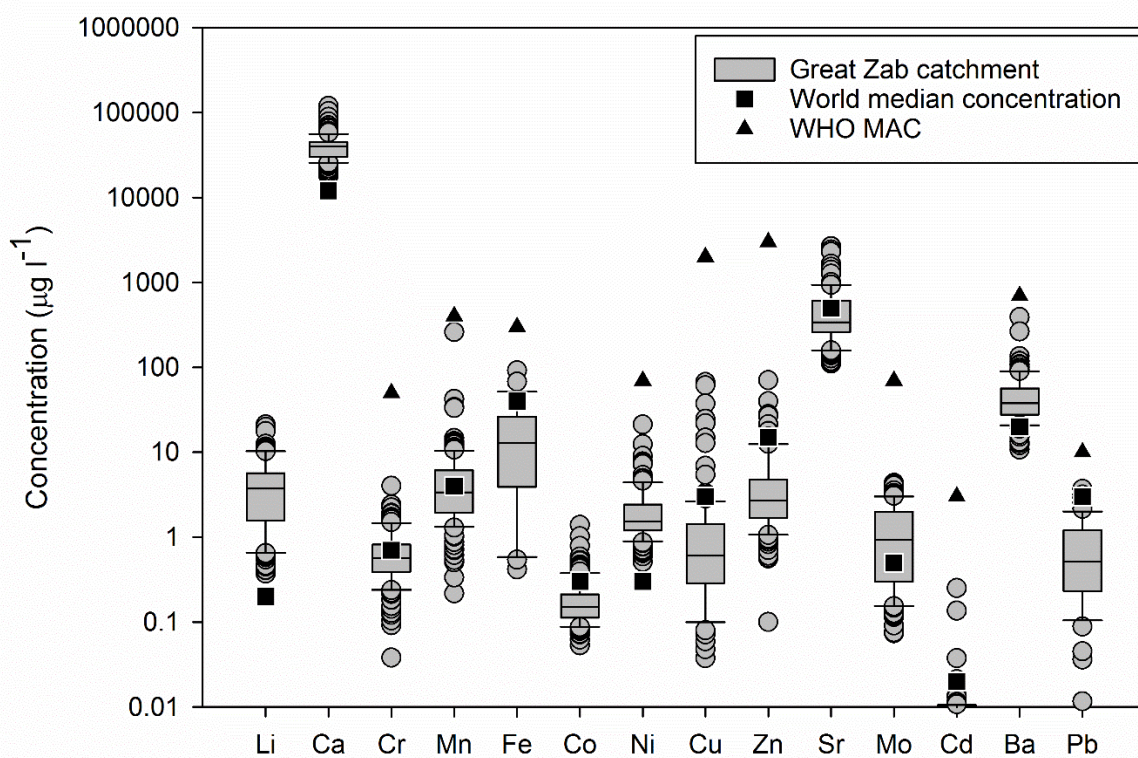


Figure 2

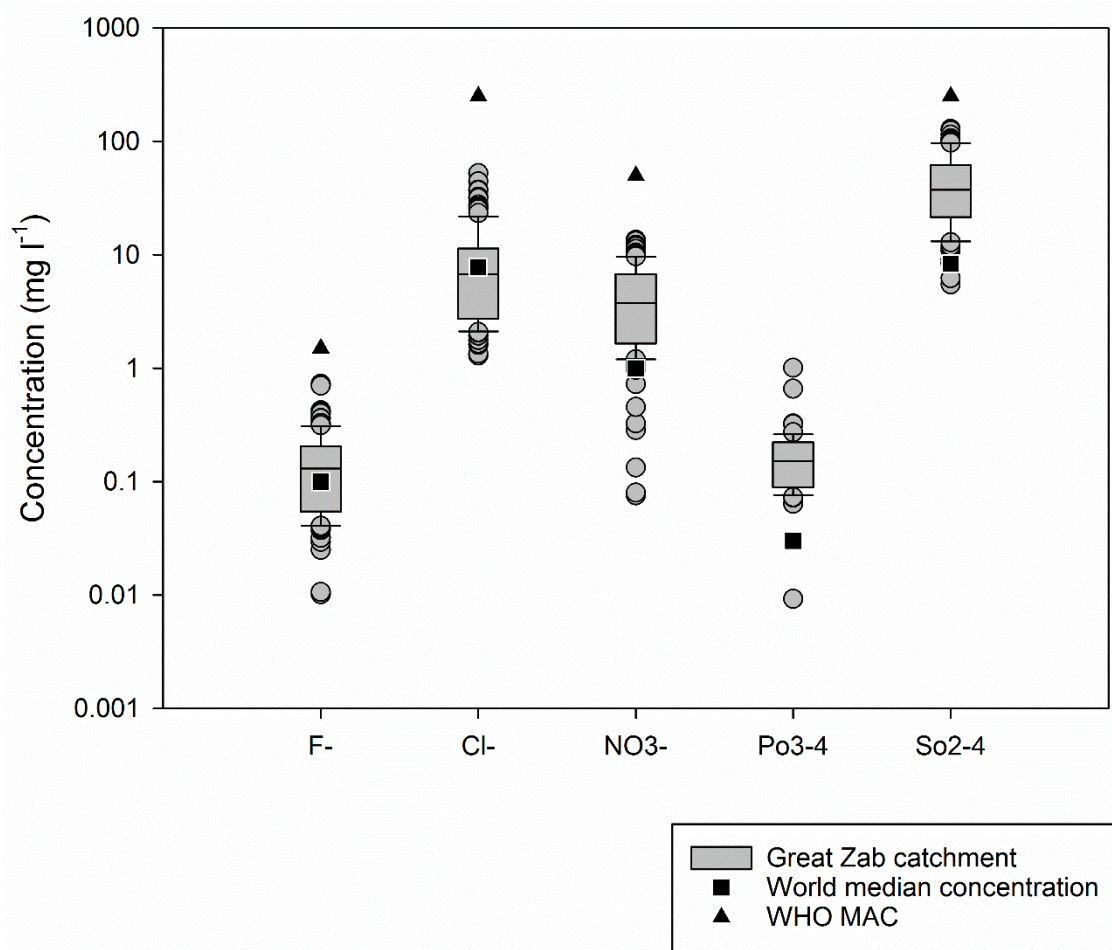


Figure 3

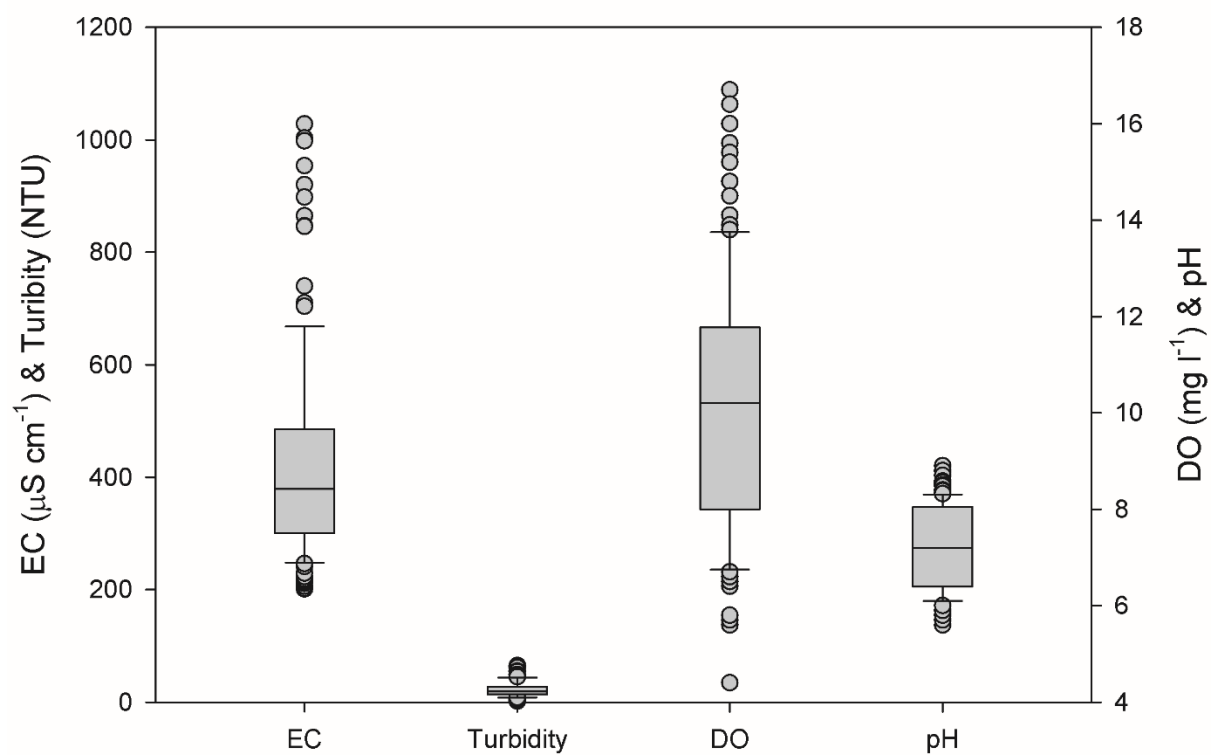


Figure 4

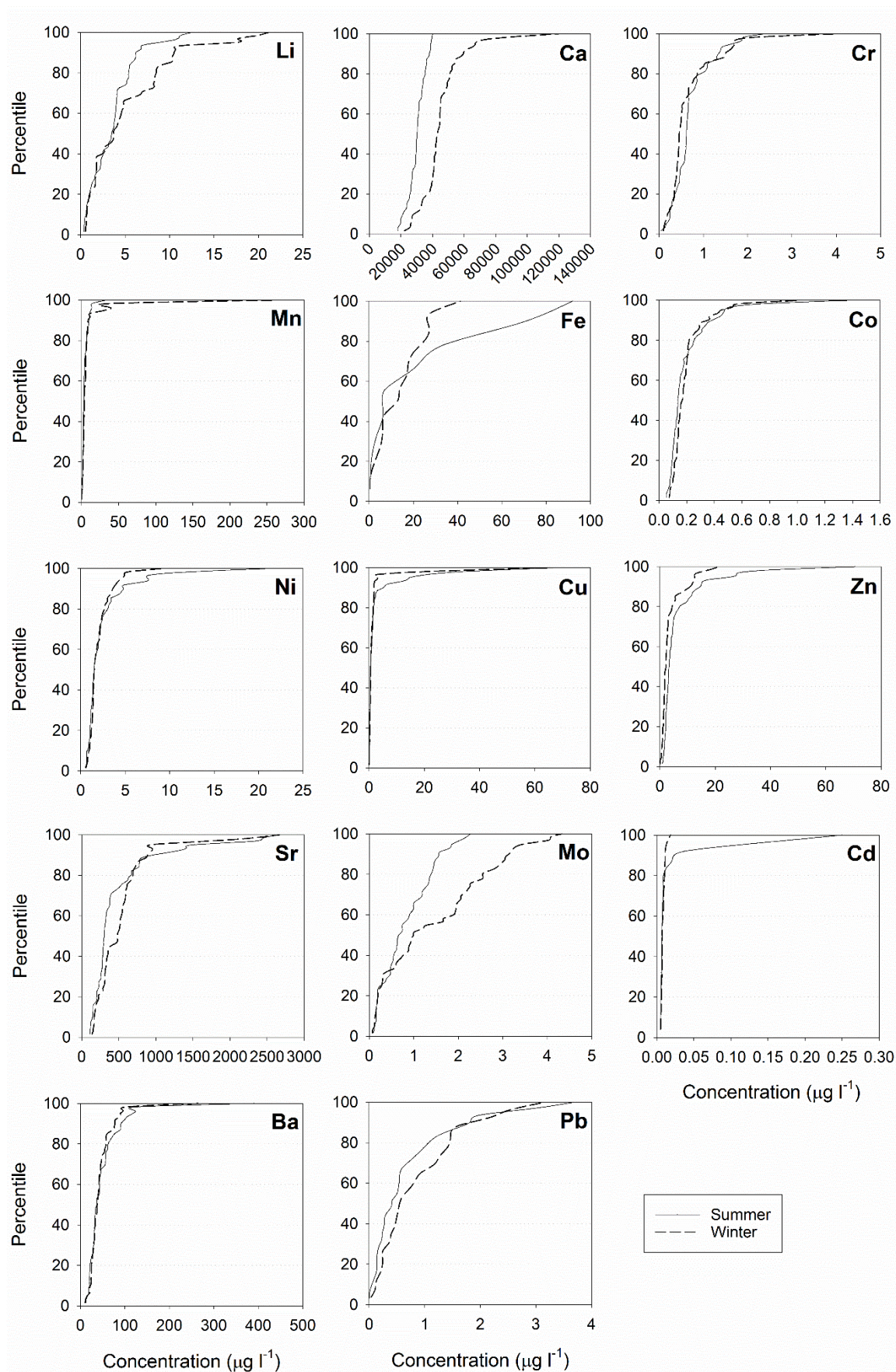


Figure 5

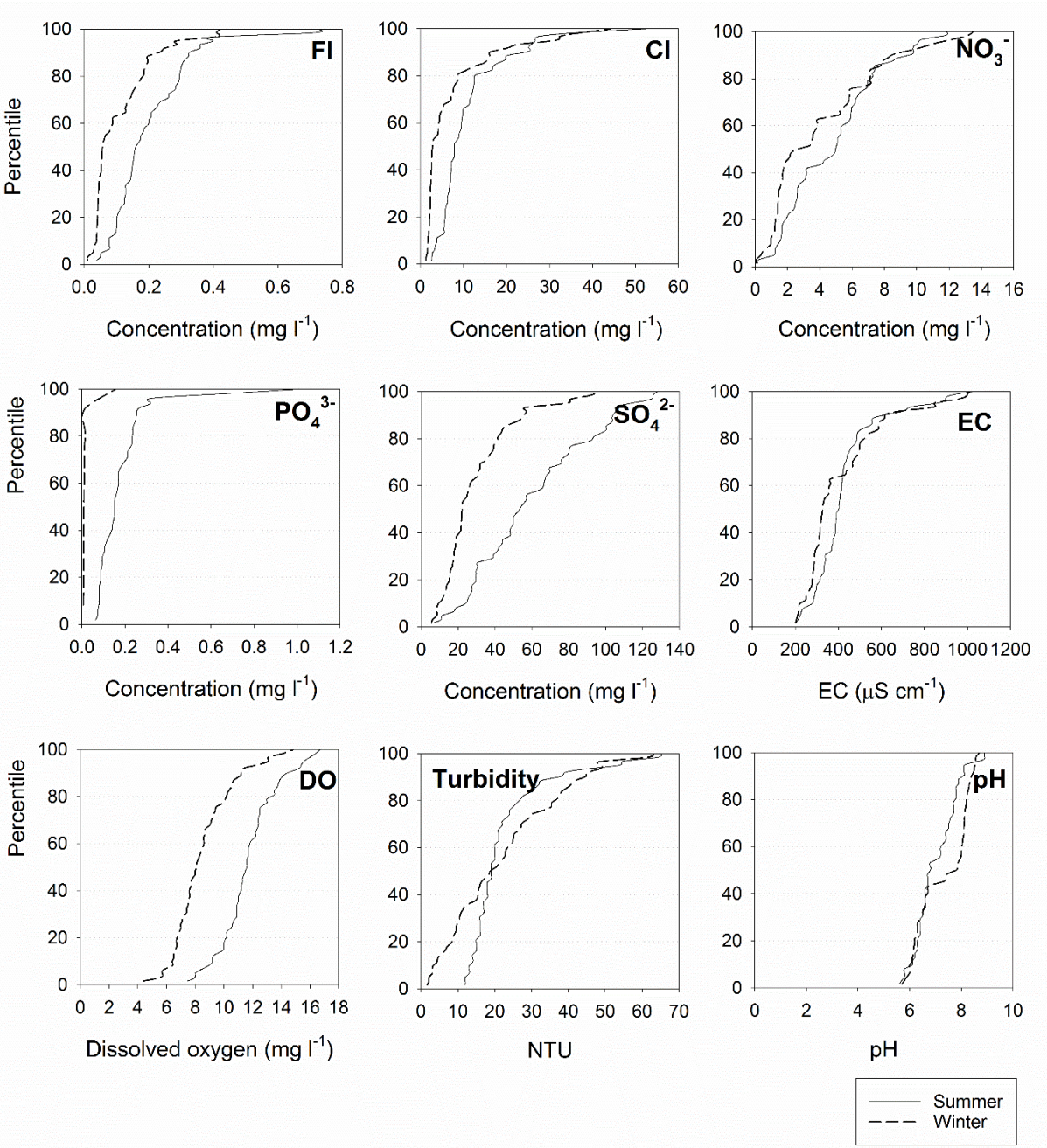


Figure 6

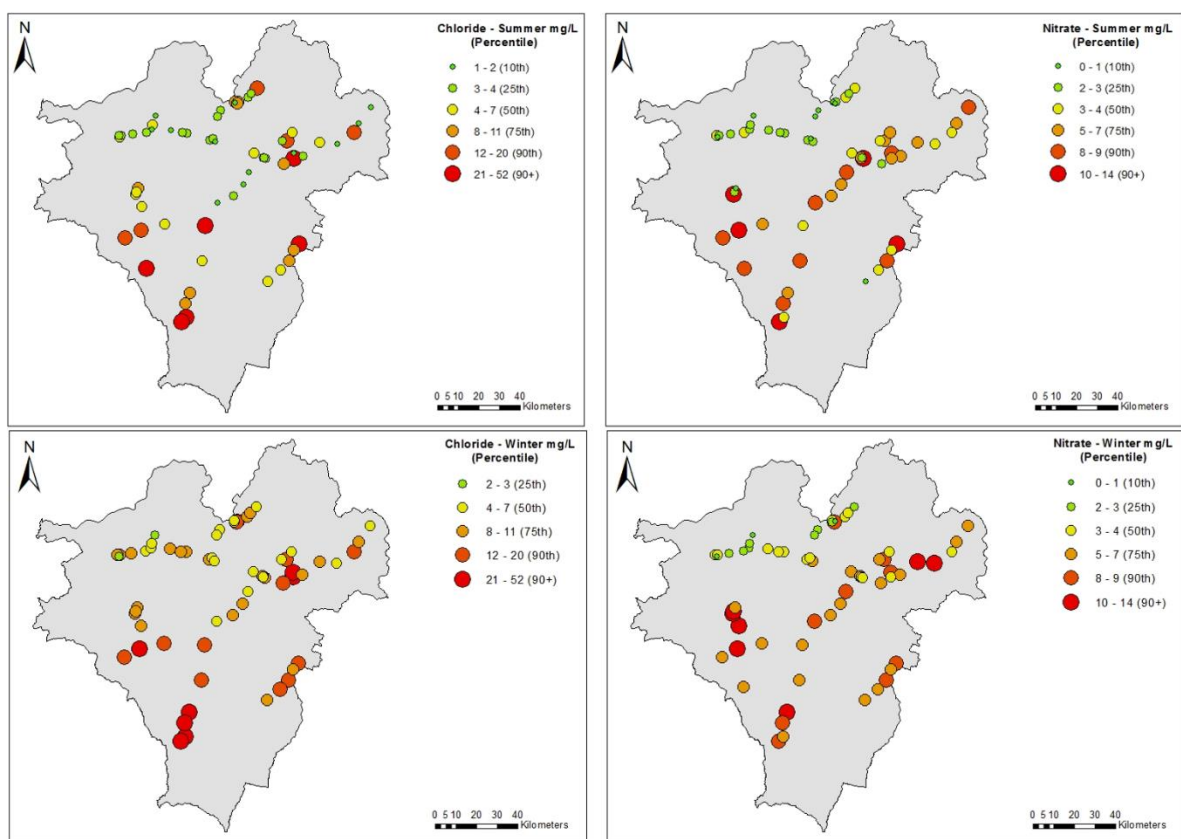


Figure 7

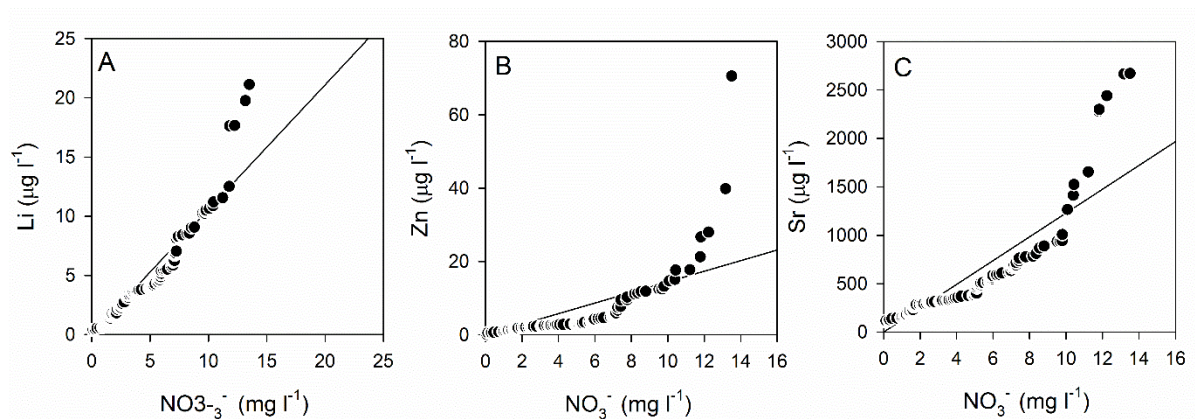


Figure 8

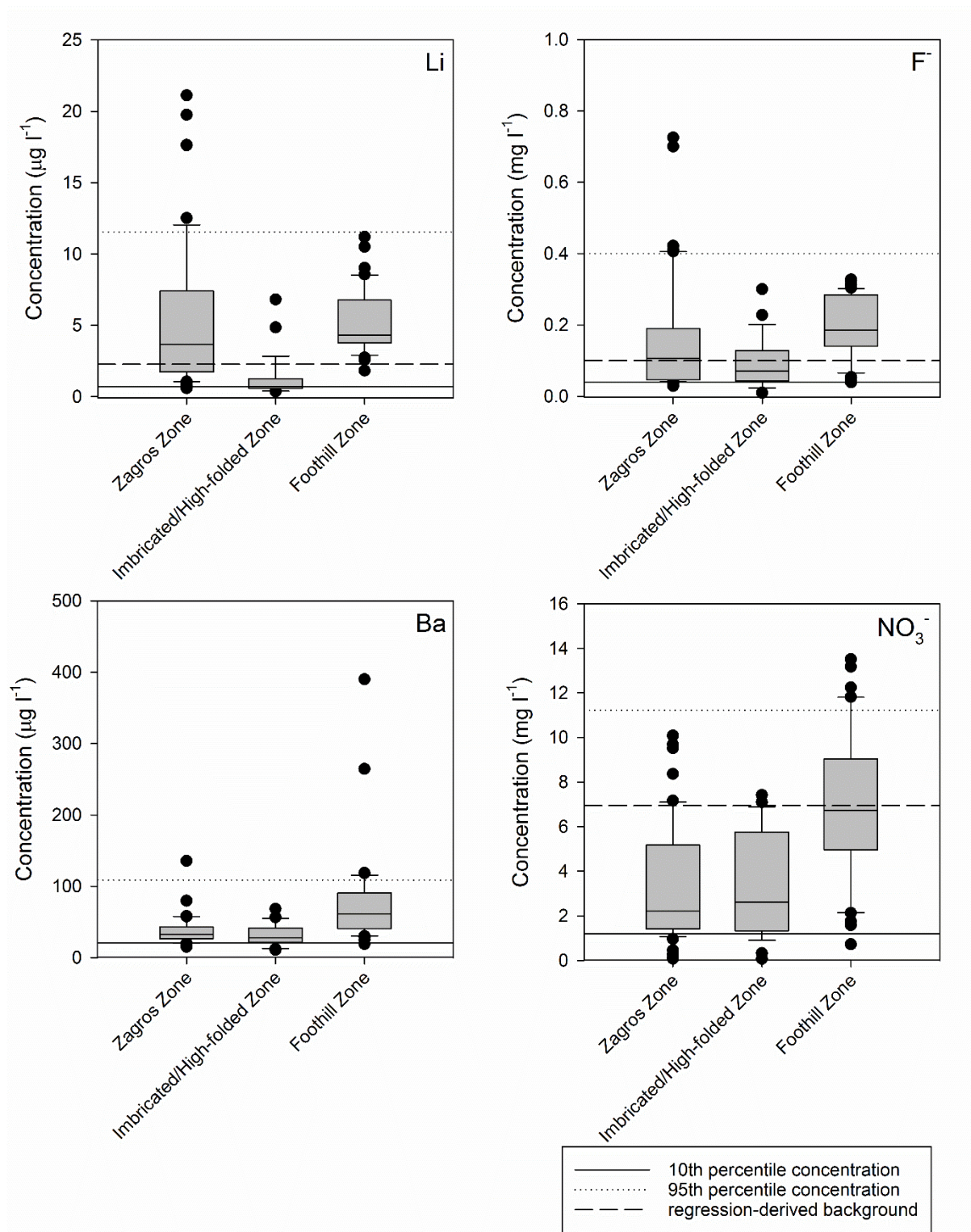


Figure 9